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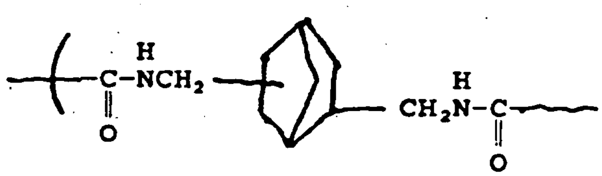

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(57) Abstract

A liquid curable resin composition comprising a urethane (meth)acrylate obtained by the reaction of a polyol, a diisocyanate, and a (meth)acrylate containing a hydroxyl group, and having a structural unit represented by formula (1). The composition has a low viscosity, exhibits excellent coatability, and produces cured product having superior durability and, particularly, free from coloration due to heat or lights. When used as a coating material for woods, plastic materials, and the like, the composition not only exhibits high productivity due to its excellent coatability, but also ensures coatings with prolonged durability.

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LIQUID CURABLE RESIN COMPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a liquid curable resin composition producing cured products which are free from yellowing and excellent in durability.

Description of the Prior Art

In the production of optical fiber, a resin coating is provided for protection and reinforcement immediately after spinning molten glass fiber. A known structure of the resin coating consists of a primary coating layer of a flexible resin which is coated on the surface of optical fiber and a secondary coating layer of a rigid resin which is provided over the primary coating layer. A so-called optical fiber ribbon is known in the art in the application of optical fiber. The optical fiber ribbon is made from several such elemental optical fibers, e.g. four or eight optical fibers, by arranging these optical fibers in a plane and fixing them with a binder to produce a ribbon structure with a rectangular cross section. The resin composition for forming the primary coating is called a soft material; the resin composition for forming the secondary coating is called a hard material; and the binder for preparing the optical fiber ribbon from several elemental optical fibers is called a ribbon material.

As laying of optical fiber cables develops in wide variety of environments in recent years, higher durability is demanded for coating materials of optical fiber, such as soft materials, hard materials, and ribbon materials. The characteristics required for curable resins used as the coating materials for optical fiber include: to be a liquid at ambient tem-

perature and have a sufficiently low viscosity to be excellently coated; to provide good productivity at a high curing rate; to have sufficient strength and superior flexibility; to exhibit very little physical change during temperature changes over a wide range; to have superior heat resistance and superior resistance to hydrolysis; to show superior long term reliability with little physical changes over time; to show superior resistance to chemicals such as acids and alkalis; to exhibit low moisture and water absorption; to exhibit superior light resistance; to exhibit high resistance to oils; and to produce little hydrogen gas which adversely affects optical fiber characteristics.

In addition, as mentioned above, along with expanding laying of optical fiber cables in recent years, higher durability is demanded for these coating materials. In particular, when the coating materials for optical fibers have poor durability and are remarkably colored during the use, it is difficult to distinguish an optical fiber from another optical fiber by the color. Maintenance of the cables would be thereby hindered. The difficulty in visual recognition of optical fibers occurs not only when ribbon materials are colored, but also when soft materials and hard materials are colored.

Along with the increased demand of optical fibers, it has become necessary to apply coat materials at a higher speed and in a stable manner. To apply the coat materials at a higher speed and in a more stable manner, the viscosity of these materials must be lower than the viscosity of conventional coating materials.

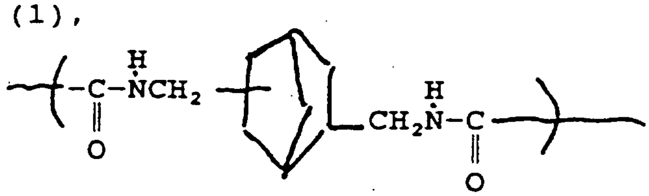
Accordingly, an object of the present invention is to provide a material which satisfies these requirements, that is, a material which has a low viscosity, exhibits excellent coatability, and produces cured product having superior durability and, particularly, free from coloration due to heat or

lights.

Another object of the present invention is to provide a liquid curable resin composition suitable as a coating material for optical fiber.

SUMMARY OF THE INVENTION

These objects of the present invention are achieved in the present invention by a liquid curable resin composition comprising a urethane (meth)acrylate obtained by the reaction of a polyol, a diisocyanate, and an acrylate containing a hydroxyl group, and having a structural unit represented by the following formula (1),

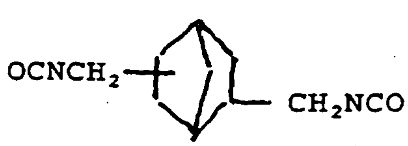


(1)

other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The structural unit of formula (1) possessed by the urethane (meth)acrylate used in the present invention can be derived from the diisocyanate of the following formula (2),



(2)

that is, from 2,5-bis(isocyanatemethyl)bicyclo[2.2.1]-heptane and/or 2,6-bis(isocyanatemethyl)bicyclo[2.2.1]-heptane, also called norbornene diisocyanate.

This urethane (meth)acrylate can be obtained by reacting a polyol, one of the diisocyanates of formula (2), and a (meth)acrylate having a hydroxyl group, specifically, by reacting the isocyanate group of the diisocyanate with each of the hydroxyl groups of the polyol and the (meth)acrylate having a hydroxyl group.

The reaction can be carried out, for example, by the following methods: a method simultaneously reacting the polyol, the diisocyanate, and the (meth)acrylate having a hydroxyl group; a method reacting the polyol and the diisocyanate to obtain an intermediate, and reacting this intermediate with the (meth)acrylate having a hydroxyl group; a method reacting the (meth)acrylate having a hydroxyl group and the diisocyanate, and then reacting the resulting compound with the polyol; a method reacting the (meth)acrylate having a hydroxyl group and the diisocyanate, reacting the resulting compound with the polyol, then again reacting with the (meth)acrylate having a hydroxyl group.

Examples which can be given of the polyol used in these reactions include diols, triols, and tetraols. Given as specific examples of the diol are polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyetherdiol obtained by ring-opening copolymerization of two or more types of ionic-polymerizable cyclic compounds.

Examples of ionic-polymerizable cyclic compounds include cyclic ethers such as ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide, 3,3-bischloromethyloxetane, tetrahydrofuran, dioxane, trioxane, tetraoxane, 3-methyltetrahydrofuran, 2-methyltetrahydrofuran, cyclohexene oxide, styrene oxide, epichlorohydrine, glycidyl methacrylate, allyl

glycidyl ether, allylglycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidylbenzoate.

It is also possible to use a polyether diol obtained by the ring-opening copolymerization of the above-mentioned ionic polymerizable compounds and cyclic imines such as ethyl imine; cyclic lactones such as β-propiolactone and glycolic acid lactide; or cyclic siloxanes such as dimethylcyclopolysiloxane.

Specific examples of combinations of the two or more types of ionic-polymerizable cyclic compounds which can be given include tetrahydrofuran and propylene oxide; tetrahydrofuran and 2-methyltetrahydrofuran; tetrahydrofuran and 3-methyltetrahydrofuran; tetrahydrofuran and ethylene oxide; propylene oxide and ethylene oxide; butene-1 oxide and ethylene oxide; and ternary polymer of tetrahydrofuran, butene-1-oxide and ethylene oxide. The ring-opening copolymers of these ionic-polymerizable cyclic compounds may be bonded at random or in blocks.

Examples of these polyether diols which are commercially available include PTMG1000 and PTMG2000 (Mitsubishi Chemical Co., Ltd.); PPG1000, EXCENOL 2020, EXCENOL 1020 (Asahi Oline); PEGIOOO, UNISAFE DC1100, UNISAFE DC1800 (Nippon Oil and Fats Co., Ltd.); PPTG2000, PPTG1000, PTG400, PTGL2000 (Hodogaya Chemical Co., Ltd.); and Z-3001-4, Z-3001-5, PBG2000A, PBG2000B (Daiichi Kogyo Seiyaku Co., Ltd.).

Beside these polyether diols, polyester diols, polycarbonate diols, polycaprolactone diols, diols of a linear hydrocarbon, cyclic diols, and the like can be used as the diol compound in the present invention. These diols other than polyether diols can be used either independently or in combination with the

polyether diols.

Examples of the polyester diols include polyester diols obtained by the reaction of a polyhydric alcohol, such as ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, 3-methyl-1,5-pentane diol, 1,9-nonane diol, or 2-methyl-1,8-octane diol, and a polybasic acid, such as phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, or sebacic acid. Commercially available products which can be used include, for example, Kurapole P-2010, PMIPA, PKA-A, PYA-A2, and PNA-2000 (Kuraray Co.).

Polycarbonate of polytetrahydrofuran and polycarbonate of 1,6-hexane diol, and commercially available products, such as DN-980, DN-981, DN-982, DN-983 (Nihon Polyurethane), PC-8000 (PPG of the US), and PC-THFCD (BASF) can be given as examples of the polycarbonate diol.

Given as examples of the polycaprolactone diol are polycaprolactone diols obtained by the reaction of ε-caprolactone and a divalent alcohol, such as ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,2-polybutylene glycol, 1,6-hexane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, and 1,4-butane diol. These polycaprolactone diols can be also commercially available under the trademarks such as PLACCEL 205, 205AL, 212, 212AL, 220, 220AL (Daicell Co., Ltd.).

Further, given as examples of the linear hydrocarbon diols are ethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane dial, and neopentyl glycol. Although the linear hydrocarbon diols can be used independently, it is

desirable for obtaining an adequate elasticity to use the linear hydrocarbon diols together with the polyether diol, polyester diol, or polycarbonate diol.

Included in the examples of the cyclic diols are 1,4-cyclohexane dimethanol, ethylene oxide addition diol to bisphenol A, butylene oxide addition diol to bisphenol A, ethylene oxide addition diol to bisphenol F, butylene oxide addition diol to bisphenol F, ethylene oxide addition diol to hydrogenated bisphenol A, butylene oxide addition diol to hydrogenated bisphenol A, ethylene oxide addition diol to hydrogenated bisphenol F, butylene oxide addition diol to hydrogenated bisphenol F, dimethylol compounds of dicyclopentadiene, and tricyclodecane dimethanol. Diols having a cyclic structure are preferably used when high elasticity of the products at high temperatures is required. Preferred diols having a cyclic structure among these compounds are ethylene oxide addition diol to bisphenol A and tricyclodecane dimethanol. These cyclic diols can be commercially available under the trademarks of DA400, DA700, DA1000 (Nippon Oil and Fats Co.), Tricyclodecanedimethanol (Mitsubishi Chemical Co.).

Other diol compounds may be used either independently or in combination with the diols mentioned above. Given as examples of such other diols are β-methyl-δ-valerolactone, polybutadiene with hydroxyl terminal groups, hydrogenated polybutadiene with hydroxyl terminal groups, castor oil-denatured diol, polydimethylsiloxane with terminal diols, and polydimethylsiloxane carbitol-denatured diols.

As the triols, trimethylolpropane, ethylene oxide adducts of trimethylolpropane, propylene oxide adducts of trimethylolpropane, butylene oxide adducts of trimethylolpropane, glycerine, ethylene oxide adducts of glycerine, propylene oxide adducts of glycerine, and butylene oxide adducts of glycerine can

be given as examples.

As the tetraols, pentaerythritol, ethylene oxide adducts of pentaerythritol, propylene oxide adducts of pentaerythritol, butylene oxide adducts of pentaerythritol, glycerine, tetrahydroxy isopropylethylenediamine, and the like can be given as examples.

Diols are preferred among these polyols. The diols, triols, and tetraols may be used either individually or in combination.

Diamines may be used together with the polyols. Examples of the diamines which can be used include ethylene diamine, tetramethylene diamine, hexamethylene diamine, paraphenylene diamine, 4,4'-diaminodiphenylmethane, diamines containing a hetero atom, and polyether diamines.

Diisocyanates other than those having the above formula (2) can be used in combination with the diisocyanate of formula (2). Examples of such other diisocyanates include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, methylene bis(4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate, bis(2-isocyanate-ethyl) fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, lysine diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate, and tetramethylxylylene diisocyanate.

Among these diisocyanates, 2,4-tolylene diisocyanate, isophorone diisocyanate, and xylylene diisocyanate, methylene bis(4-cyclohexylisocyanate), are particularly preferred.

The amount of these diisocyanates other than the diisocyanates of formula (2) is preferably about 50% by weight or smaller of the total amount of diisocyanates. If more than about 50% by weight, the effects of the low viscosity and high durability may be decreased.

Examples of a (meth)acrylate having a hydroxyl group used in the present invention include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxyalkyl(meth)acryloyl phosphate, 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, (meth)acrylates represented by the following structural formulas (3) or (4),

$$CH_2{=}C(R^1){-}COOCH_2CH_2{-}(OCOCH_2CH_2CH_2CH_2CH_2)_n{-}OH \qquad (3)$$

$$CH_2{=}C(R^1){-}COOCH_2CH_2{-}(OH)CH_2{-}O{-}(C_6H_5) \qquad (4)$$

wherein R^1 is a hydrogen atom or a methyl group and n denotes an integer of 1-15. In addition, compounds obtained by an addition reaction between a compound containing a glycidyl group, such as, alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate, and (meth)acrylic acid can also be used.

Among these (meth)acrylates having a hydroxyl group, particularly desirable are 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate.

The polyol, the diisocyanate, and the (meth)acrylate containing a hydroxyl group are used preferably in a proportion such that about 1.1-3

equivalents of the diisocyanate group contained in the diisocyanate compounds and about 0.2-1.5 equivalents of the hydroxyl group contained in the (meth)acrylate are used for one equivalent of the hydroxyl group of the polyol. It is desirable that the hydroxyl groups in the polyol and the (meth)acrylate are almost equivalent to the isocyanate groups in the diisocyanate compound.

It is possible to replace a portion of the (meth)acrylate containing a hydroxyl group with a compound having a functional group which can add to isocyanate group. γ-mercaptotrimethoxy silane and γ-aminotrimethoxy silane are given as examples of the compound having such a functional group. Adhesion to materials such as glass can be improved by using such a compound.

In the reaction between the polyol, the diisocyanate, and the (meth)acrylate containing a hydroxyl group, a urethanization catalyst such as copper naphthenate, cobalt naphthenate, zinc naphthenate, n-butyl-tin dilaurylate, triethylamine, 1,4-diazabicyclo[2.2.2]octane, or 2,6,7-trimethyl-1,4--diazabicyclo[2.2.2]octane is used, generally, in an amount of about 0.01 to about 1 part by weight for 100 parts by weight of the reaction raw materials. The reaction temperature is normally in the range of about 10-90°C, preferably of about 30-80°C.

The urethane (meth)acrylate used in the present invention has a weight average molecular weight reduced to polystyrene of about 500-15,000.

The urethane (meth)acrylate having the structural unit of formula (1) thus obtained is incorporated in the composition in an amount of about 10-90% by weight. The amount of about 20-70% by weight is more preferred, especially in the case where coatability to the optical fiber and flexibility and long-term reliability of the coatings after cure are desired.

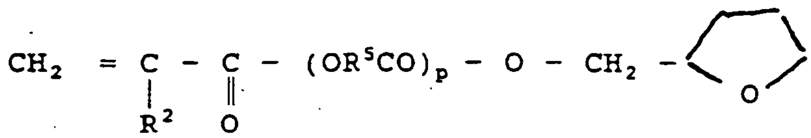
Besides these components, a urethane di(meth)acrylate, which can be obtained by reacting two mols of urethane (meth)acrylate containing a hydroxyl group with one mol of diisocyanate, can be incorporated to the liquid curable resin composition of the present invention. Given as examples of such a urethane di(meth)acrylate are the reaction product of hydroxyethyl (meth)acrylate and the diol of the formula (2), the reaction product of hydroxyethyl (meth)acrylate and 2,4-tolylene diisocyanate, the reaction product of hydroxyethyl (meth)acrylate and isophorone diisocyanate, the reaction product of hydroxypropyl (meth)acrylate and 2,4-tolylene diisocyanate, and the reaction product of hydroxypropyl (meth)acrylate and isophorone diisocyanate. These urethane di(meth)acrylate may be added in an amount of smaller than 30% by weight of the total amount of the composition.

Polymerizable monofunctional vinyl monomers or polymerizable polyfunctional monomers can be added to the urethane (meth)acrylate of the liquid curable resin composition of the present invention. Examples of the polymerizable monofunctional vinyl monomers include lactams containing a vinyl group, such as N-vinyl pyrrolidone and N-vinyl caprolactam; alicyclic (meth)acrylates, such as isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, and cyclohexyl (meth)acrylate; benzyl (meth)acrylate, 4-butylcyclohexyl (meth)acrylate; (meth)acryloyl morpholine, vinyl imidazole, and vinyl pyridine. Other examples of the monofunctional compounds are 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-hydroxybutyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, isobutyl

(meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, benzyl (meth)acrylate, phenoxyethyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxypolypropylene glycol (meth)acrylate, diacetone (meth)acrylamide, isobutoxymethyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, t-octyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl (meth)acrylate, N,N-diethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, hydroxybutyl vinyl ether, lauryl vinyl ether, cetyl vinyl ether, 2-ethylhexyl vinyl ether; and compounds represented by the following formulas (5) to (7).

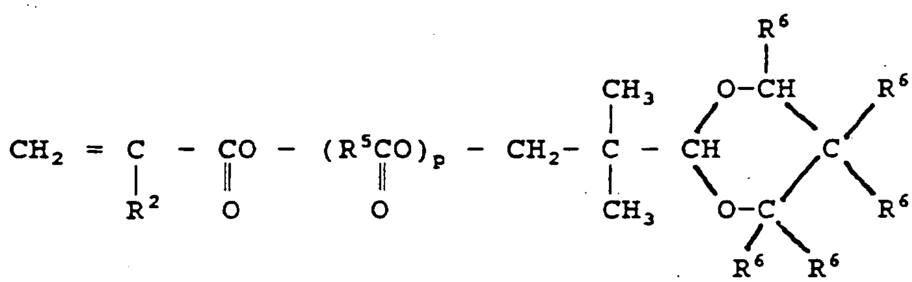
$$CH_2=C(R^2)-COO(R^3O)_m-R^4 \qquad (5)$$

wherein R^2 is a hydrogen atom or a methyl group; R^3 is an alkylene group containing 2 to 6, preferably 2 to 4 carbon atoms; R^4 is a hydrogen atom or an alkyl group containing 1 to 12, preferably 1 to 9, carbon atoms; and m is an integer from 0 to 12, and preferably from 1 to 8.



(6)

wherein R^2 is the same as defined above; R^5 is an alkylene group containing 2 to 8, preferably 2 to 5, carbon atoms; and p is an integer from 1 to 8, and preferably from 1 to 4.



(7)

wherein R^2, R^5, and p are the same as defined above; and R^6s are individually a hydrogen atom or a methyl group. Commercially available monofunctional compounds include ARONIX M111, M113, M114, M117 (Toagosei Chemical Industry Co., Ltd.), KAYARAD DTC110S, R629, R644 (Nippon Kayaku Co., Ltd.), and Viscoat 3700 (Osaka Organic Chemical Industry, Ltd.).

Examples of the polyfunctional compounds include: trimethylolpropane tri(meth)acrylate, pentaerythritol (meth)acrylate, ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycoldi(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropanetrioxyethyl (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, and di(meth)acrylate of a diol which is an ethylene oxide or propylene oxide adduct to bisphenol A, di(meth)acrylate of a diol which is an ethylene oxide

or propylene oxide adduct to hydrogenated bisphenol A, epoxy (meth)acrylate which is a (meth)acrylate adduct to diglycidyl ether of bisphenol A, and triethylene glycol divinyl ether. Given as commercially available polyfunctional compounds are YUPIMER-UV, SA1002, SA2007 (Mitsubishi Chemical Co., Ltd.), Viscoat 700 (Osaka Organic Chemical Industry Ltd.), KAYARAD R-604, DPCA-20, DPCA-30, DPCA-60, DPCA-120, HX-620, D-310, D-330, (Nippon Kayaku Co., Ltd.), and ARONIX M-210, M-215, M-315, M-325 (Toagosei Chemical Industry Co., Ltd.). Among these polyfunctional compounds, tricyclo-decanedimethanol diacrylate (YUPIMER-UV, SA1002) and Viscoat 700 are preferred.

These polymerizable monomers are preferably added to the composition in an amount of about 15-80% by weight, and particularly preferably about 20-70% by weight. If this amount is less than about 15% by weight, the composition has an unduly high viscosity, which results not only in impaired coatability but also in cured products with a low tenacity and a high contraction. If this amount is more than about 80%, the curing speed is slow.

In general, at least two of said polymerizable monomers are used, in order to adjust properties of the cured coating, such as hardness, flexibility, refractive index, T_g and the like.

A polymerization initiator can be added to the liquid curable resin composition of the present invention. Either a photo-polymerization initiator or a heatpolymerization initiator may be used as the polymerization initiator.

When the liquid curable resin composition of the present invention is cured with heat, a heat-polymerization initiator, such as a peroxide or an azo compound, is usually used. Specific examples are benzoyl peroxide, t-butyloxybenzoate, and azobisisobutylonitrile. When the liquid curable resin

composition of the present invention is cured with lights, a photo-polymerization initiator, optionally in combination with a photosensitizer, is preferably used. Examples of the photo-polymerization initiator include 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanthone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide; and commercially available products, such as Irgacure 184, 369, 651, 500, 907 CGI1700, CGI1750, CGI1850, CG24-61 (Ciba Geigy), Lucirin LR8728 (BASF), Darocure 1116, 1173 (Merck Co.), and Uvecryl P36 (UCB).

Given as examples of the photo-sensitizers are triethylamine, diethylamine, N-methyldiethanolamine, ethanolamine, 4-dimethylaminobenzoic acid, methyl 4-dimethyl-aminobenzoate, ethyl 4-dimethylaminobenzoate, isoamyl 4-dimethylaminobenzoate, and commercially available products such as Uvecryl P102, P103, P104, and P105 (manufactured by UCB Co.). When the liquid curable resin composition of the present invention is cured using heat and UV lights together, the photo-polymerization initiator and the heat-polymerization initiator can be used in combination. These polymerization initiators are incorporated in the composition in an amount of about 0.1-10% by weight, and preferably about 0.5-7% by weight.

Beside the above components, the liquid

curable resin composition of the present invention may be formulated with various components, such as other curable oligomers or polymers, reactive diluents, and other additives, to the extent that the effect of the present invention is not adversely affected. Included in the examples of the other curable oligomers or polymers are polyester (meth)acrylates, epoxy (meth)acrylates, polyamide (meth)acrylates, siloxane polymers having a (meth)acryloyloxy group, and reactive monomers which are obtained by the reaction of acrylic acid and a copolymer of glycidyl (meth)acrylate and other vinyl monomer.

Beside these, various additives may be added as required, such as antioxidants, coloring dyes, UV absorbers, photo-stabilizers, silane coupling agents, heat polymerization inhibitors, leveling agents, surface active agents, preservatives, plasticizers, lubricants, solvents, filters, aging preventives, wettability improvers, and coated surface improvers. Commercially available antioxidants which can be used are Irganox 1010, 1035, 1076, 1222 (Ciba Geigy), Antigen P, 3C, FR, GA-80 (Sumitomo Chemical Industries Co., Ltd.), and the like. As UV absorbers, Tinuvin P234, P320, P326, P327, P328, P329, P213 (Ciba Geigy), Seesorb 102, 103, 501, 202, 712, 704 (manufactured by Shipro Kasei Kaisha, Ltd.) can be given. Commercially available photo-stabilizers which can be added include Tinuvin 292, 144, 622LD (manufactured by Ciba Geigy), Sanol LS770 (manufactured by Sankyo Chemical Co.), and SUMISORB TM-061 (manufactured by Sumitomo Chemical Industries). Examples of silane coupling agents which can be given are γ-aminopropyltriethoxy silane, γ-mercaptopropyltrimethoxy silane, γ-methacryloxypropyltrimethoxy silane, and commercially available products such as SH6062, SZ6030 (Toray Silicone Co.) and KBE903, KBE603, KBE403 (Shin-etsu Silicone Co.).

The viscosity of the liquid curable resin

composition of the present invention is normally in the range of about 200 to about 20,000 dPa.s at 25°C, and preferably about 2,000 to about 15,000 dPa.s at 25°C. When the composition is used as a ribbon material or secondary coating for optical fiber, the Young's modulus of the composition after it has been cured is normally about 10-250 kg/mm^2, and preferably about 40-150 kg/mm^2. When used as a primary coating for optical fibers, the cured product preferably has a Young's modulus of about 0.05-0.3 kg/mm^2.

The liquid curable resin composition of the present invention is cured by heat and/or radiation. Here, the radiation means radiations such as infrared lights, visible lights, ultraviolet lights, X-rays, electron beams, α-rays, β-rays, and γ-rays.

The present invention will be hereinafter described in more detail by way of examples which are given for illustration of the present invention and shall not to be construed as limiting the present invention. In the examples hereinafter "part(s) by weight" is simply described as "part(s)".

EXAMPLES

Preparation of urethane acrylate (1)

3.6 parts of a 50:50 (by weight) mixture of 2,5-bis(isocyanatemethyl)bicyclo[2.2.1]heptane and 2,6-bis(isocyanatemethyl)bicyclo[2.2.1]heptane (hereinafter called NBDI), 50.5 parts of a ring-opening copolymer of ethylene oxide and butene oxide having a number average molecular weight of 4,000, and 0.01 part of 2,6-di-tert-butyl-p-cresol, as a polymerization inhibitor, were placed in a reaction vessel equipped with a stirrer. While stirring, the mixture was cooled with ice to below 10°C, whereupon 0.04 part of dibutyltin dilaurate was added. The mixture was stirred for 2 hours while controlling the temperature at 20-30°C.

After the addition of 0.3 part of γ-mercaptopropyltrimethoxy silane, the mixture was stirred for 1 hour at 30-40°C. Then, 1.2 parts of hydroxyethyl acrylate was added and the mixture was stirred for a further 4 hours at 50-60°C. The reaction was terminated when the amount of residual isocyanate was below 0.1% by weight. The liquid of the urethane acrylate resin thus obtained is referred to as UA-1.

Preparation of urethane acrylate (2)

6.5 parts of NBDI, 42.0 parts of a ring-opening copolymer of tetrahydrofuran and 3-methyltetrahydrofuran having a number average molecular weight of 2,000, and 0.01 part of 2,6-di-tert-butyl-p-cresol, as a polymerization inhibitor, were placed in a reaction vessel equipped with a stirrer. While stirring, the mixture was cooled with ice to below 10°C, whereupon 0.04 part of dibutyltin dilaurate was added. The mixture was stirred for 2 hours while controlling the temperature at 20-30°C. After the addition of 2.2 parts of hydroxyethyl acrylate, the mixture was stirred for a further 4 hours at 50-60°C. The reaction was terminated when the amount of residual isocyanate was below 0.1% by weight. The liquid of the urethane acrylate resin thus obtained is referred to as UA-2.

Preparation of urethane acrylate (3)

6.5 parts of NBDI, 42.0 parts of a ring-opening copolymer of ethylene oxide and butene oxide having a number average molecular weight of 2,000, and 0.01 part of 2,6-di-tert-butyl-p-cresol, as a polymerization inhibitor, were placed in a reaction vessel equipped with a stirrer. While stirring, the mixture was cooled with ice to below 10°C, whereupon 0.04 part of dibutyltin dilaurate was added. The mixture was stirred for 2 hours while controlling the

temperature at 20-30°C. After the addition of 2.2 parts of hydroxyethyl acrylate, the mixture was stirred for a further 4 hours at 50-60°C. The reaction was terminated when the amount of residual isocyanate was below 0.1% by weight. The liquid of the urethane acrylate resin thus obtained is referred to as UA-3.

Examples 1-8

<Preparation of liquid curable resin compositions>

Liquid compositions for coating as the upper layer of optical fibers were prepared from the components shown in Table 1, by charging these components to a reaction vessel equipped with a stirrer and stirring the mixture for 3 hours at 50-60°C.

TABLE 1

Component (part by weight)	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
UA-1	55	55	55	0	0	0	0	0
UA-2	0	0	0	50	50	0	0	0
UA-3	0	0	0	0	0	50	50	50
M113™	15	15	15	20	20	20	20	15
M114™	0	17	0	0	0	0	0	15
IBXA	21	0	0	14	0	14	0	0
M600A™	0	0	14	0	14	0	14	4
Vcap	6	3	6	6	6	6	6	6
LA	0	7	7	7	0	7	7	7
Lucirin™	1.5	1.5	0	1.5	0	1.5	0	1.5
BAPO	0	0	1.5	0	1.5	0	1.5	0
Irganox1035™	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

M113, M114: Polymerizable monomers, Aronix M113 and M114 manufactured by Toagosei Chemical Industry

IBXA: Isobornyl acrylate

M600A: 2-Hydroxy-3-phenoxypropyl acrylate, a polymerizable monomer manufactured by Kyoeisha Chemical Co.

Vcap: N-vinyl caprolactam, a polymerizable monomer

Footnote for Table 1 (continued)

LA:	Lauryl acrylate, a polymerizable monomer manufactured by Kyoeisha Chemical Co.
BAPO:	Bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, a photo-polymerization initiator
Lucirin:	2,4,6-Trimethylbenzoyldiphenylphosphine oxide, a photo-polymerization initiator manufactured by BASF
Irganox 1035:	Antioxidant manufactured by Ciba-Geigy

<u>Preparation of urethane acrylate (4)</u>

19.5 parts of NBDI, 0.06 part of dibutyltin dilaurate, 0.015 part of 2,6-di-tert-butyl-p-cresol, and 11.9 parts of tricyclodecanedimethanol diacrylate were placed in a reaction vessel equipped with a stirrer and cooled to 15°C or lower. 15.25 parts of hydroxyethyl acrylate was added dropwise while stirring and controlling the temperature at 30°C or lower. After the addition, the mixture was reacted for 1 hour at 30°C. Then, 2.64 parts of tricyclodecanedimethanol and 28.5 parts of a ringopening copolymer of tetrahydrofuran and 3-methyltetrahydrofuran having a number average molecular weight of 2,000 were added and the mixture was stirred at 20-55°C. The reaction was terminated when the amount of residual isocyanate was below 0.1% by weight. To the resulting reaction mixture were added 7.95 parts of N-vinylpyrrolidone, 6.74 parts of isobornyl acrylate, 3.45 parts of tricyclodecane-dimethanol diacrylate, 0.3 part of Irgacure 1035 (manufactured by Ciba Geigy), and 0.14 part of 2,6-di-tert-butyl-p-cresol, and the mixture was stirred while controlling the temperature at 50-60°C until a homogeneous, transparent liquid was obtained. This transparent liquid of urethane acrylate resin is referred to as UA-4.

Preparation of urethane acrylate (5)

16.6 parts of NBDI, 0.08 part of dibutyltin dilaurate, 0.02 part of 2,6-di-tert-butyl-p-cresol, 7.7 parts of N-vinylpyrrolidone, and 15.5 parts of tricyclodecanedimethanol diacrylate were placed in a reaction vessel equipped with a stirrer and cooled to 5-10°C. 5.8 parts of hydroxyethyl acrylate was added dropwise while stirring and controlling the temperature at 10°C or lower. After the addition, the mixture was reacted for 1 hour at 30°C. Then, 1.7 parts of ethylene glycol and 54.7 parts of polytetramethylene glycol having a number average molecular weight of 2,000 were added and the mixture was reacted at 30-50°C for 2 hours. After the addition of 0.5 parts of hydroxyethyl acrylate, the reaction was continued at 50-60°C and terminated when the amount of residual isocyanate was below 0.1% by weight, thus obtaining urethane acrylate UA-5.

Preparation of urethane acrylate (6)

12.2 parts of NBDI, 0.013 part of dibutyltin dilaurate, 0.009 part of 2,6-di-tert-butyl-p-cresol, 13.7 parts of isobornyl acrylate were placed in a reaction vessel equipped with a stirrer and cooled to 5-10°C. 13.7 parts of hydroxyethyl acrylate was added dropwise while stirring and controlling the temperature at 40°C or lower. After the addition, the mixture was reacted for 1 hour at 45-55°C. The reaction was terminated when the amount of residual isocyanate was below 0.1% by weight. To the resulting reaction mixture were added 2.6 parts of N-vinylpyrrolidone, 5.9 parts of tricyclodecanedimethanol diacrylate, 0.3 part of Irganox 1035 (manufactured by Ciba Geigy), 50.3 parts of UA-5, and 0.3 part of diethylamine, followed by stirring at 40-50°C to obtain a homogeneous, transpar nt liquid. This transparent liquid of urethane acrylate resin is referred to as UA-6.

Examples 9-12

<Preparation of liquid curable resin compositions>

Liquid compositions for coating secondary, upper layer were prepared from the components shown in Table 2, by charging these components to a reaction vessel equipped with a stirrer and stirring the mixture for 3 hours at 50-60°C.

TABLE 2

Component	Example 9	Example 10	Example 11	Example 12
UA-4	97	0	98	0
UA-6	0	97	0	98
Irgacure 184	3	3	0	0
Lucirin	0	0	1.5	1.5
Irgacure 907	0	0	0.5	0.5

Irgacure 184: 1-Hydroxycyclohexyl phenyl ketone (a photo-polymerization initiator)

Irgacure 907: 2-Methyl-1-[4-(methylthio)phenyl]-2-molphorinopropane-1-one (a photo-polymerization initiator)

Lucirin: A photo-polymerization initiator

Preparation of urethane acrylate (7)

3.0 parts of tolylene diisocyanate, 50.5 parts of a ring-opening copolymer of ethylene oxide and butene oxide having a number average molecular weight of 4,000, and 0.01 part of 2,6-di-tert-butyl-p-cresol, as a polymerization inhibitor, were placed in a reaction vessel equipped with a stirrer, cooled with ice to below 10°C while stirring. At the temperature of below 10°C, 0.04 part of dibutyltin dilaurate was added and the mixture was stirred for 2 hours while controlling the temperature at 20-30°C. Then, 0.3 part of γ-mercaptopropyltrimethoxy silane was added,

followed by stirring for 1 hour while controlling the temperature at 30-40°C. After the addition of 1.2 parts of hydroxyethyl acrylate, the reaction was continued at 50-60°C for 4 hours and terminated when the amount of residual isocyanate was below 0.1% by weight, thus obtaining urethane acrylate UA-7.

Preparation of urethane acrylate (8)

5.5 parts of tolylene diisocyanate, 42.0 parts of a ring-opening copolymer of tetrahydrofuran and 3-methyltetrahydrofuran having a number average molecular weight of 2,000, and 0.01 part of 2,6-di-tert-butyl-p-cresol, as a polymerization inhibitor, were placed in a reaction vessel equipped with a stirrer, and cooled with ice to below 10°C, while stirring. At the temperature of below 10°C, 0.04 part of dibutyltin dilaurate was added, followed by stirring for 2 hours while controlling the temperature at 20-30°C. Then, 2.2 parts of hydroxyethyl acrylate was added and the mixture was stirred for a further 4 hours at 50-60°C. The reaction was terminated when the amount of residual isocyanate was below 0.1% by weight, thus obtaining urethane acrylate UA-8.

Comparative Examples 1-4

<Preparation of comparative liquid curable resin compositions>

Liquid compositions were prepared from the components shown in Table 3, by charging these components to a reaction vessel equipped with a stirrer and stirring the mixture for 3 hours at 50-60°C.

TABLE 3

Component	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
UA-7	55	55	0	0
UA-8	0	0	50	50
M113	15	15	20	20
M114	0	17	0	0
IBXA	21	0	14	14
Vcap	6	3	6	6
LA	0	7	7	7
Lucirin	1.5	0	1.5	1.5
BAPO	0	1.5	0	0

In Table 3, M113, M114, IBXA, Vcap, LA, BAPO, and Lucirin are the same as defined for Table 1.

Preparation of urethane acrylate (9)

16.5 parts of toluene diisocyanate, 0.06 part of dibutyltin dilaurate, 0.01 part of 2,6-di-tert-butyl-pcresol, and 11.9 parts of tricyclodecanedimethanol diacrylate were placed in a reaction vessel equipped with a stirrer and cooled to below 15°C. Then, 15.25 parts of hydroxyethyl acrylate was added dropwise while stirring to control the temperature at 30°C or lower. After the addition, the mixture was reacted for 1 hour at 30°C. Then, 2.64 parts of tricyclodecane dimethanol and 28.5 parts of a ring-opening copolymer of tetrahydrofuran and 3-methyltetrahydrofuran having a number average molecular weight of 2,000 were added and the mixture was reacted at 20-55°C until the amount of residual isocyanate was below 0.1% by weight, whereupon the reaction was terminated. To the resulting reaction mixture were added 7.95 parts of N-vinylpyrrolidone, 6.74 parts of isobornyl acrylate, 3.45 parts of tricyclod canedimethanol diacrylate, 0.3 part of Irganox 1035 (manufactured by Ciba Geigy), and 0.14 part of 2,6-di-tert-butyl-p-cresol, and the mixture was stirred while controlling the temperature at 50-60°C

until a homogeneous, transparent liquid was obtained. This transparent liquid of urethane acrylate resin is referred to as UA-9.

Preparation of urethane acrylate (10)

14 parts of toluene diisocyanate, 0.08 part of dibutyltin dilaurate, 0.02 part of 2,6-di-tert-butyl-p-cresol, 7.7 parts of N-vinylpyrrolidone, and 15.5 parts of tricyclodecanedimethanol diacrylate were placed in a reaction vessel equipped with a stirrer, and cooled below 5-10°C. 5.8 parts of hydroxyethyl acrylate was added dropwise while stirring and controlling the temperature at 10°C or lower. After the addition, the mixture was reacted for 1 hour at 30°C. Then, 1.7 parts of ethylene glycol and 54.7 parts of a polytetramethylene glycol having a number average molecular weight of 2,000 were added and the mixture was reacted for 2 hours at 30-50°C. After further addition of 0.5 part of hydroxyethyl acrylate, the reaction was continued at 50-60°C and terminated when the amount of residual isocyanate was below 0.1% by weight, thus obtaining urethane acrylate UA-10.

Preparation of urethane acrylate (11)

10.3 parts of toluene diisocyanate, 0.013 part of dibutyltin dilaurate, 0.009 part of 2,6-di-tert-butyl-p-cresol, 13.7 parts of isobornyl acrylate were placed in a reaction vessel equipped with a stirrer and cooled to 5-10°C. 13.7 parts of hydroxyethyl acrylate was added dropwise while stirring to control the temperature at 40°C or lower. After the addition, the mixture was reacted for 1 hour at 45-55°C. The reaction was terminated when the amount of residual isocyanate was below 0.1% by weight. To the resulting r action mixture were added 2.6 parts of N-vinylpyrrolidone, 5.9 parts of tricyclodecanedimethanol diacrylate, 0.3 part of Irganox 1035 (manufactured by

Ciba Geigy), 50.3 parts of UA-10, and 0.3 part of diethylamine, followed by stirring at 40-50°C to obtain a homogeneous, transparent liquid. This transparent liquid of urethane acrylate resin is referred to as UA-11.

Comparative Examples 5-8

<Preparation of comparative liquid curable resin compositions>

Liquid compositions for coating secondary, upper layer were prepared from the components shown in Table 4, by charging these components to a reaction vessel equipped with a stirrer and stirring the mixture for 3 hours at 50-60°C.

TABLE 4

Component	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
UA-9	97	0	98	0
UA-11	0	97	0	98
Irgacure 184	3	3	0	0
Lucirin	0	0	1.5	1.5
Irgacure 907	0	0	0.5	0.5

In Table 4, Irgacure 184, Lucirin, and Irgacure 907 are the same as defined for Table 2.

Test Examples

The liquid curable resin compositions prepared in the above examples were cured and test leaves were prepared from the resin by the method mentioned below. The following tests were carried out to evaluate the test leaves.

(i) Preparation of test leaves

The liquid curable resin compositions were coated on glass plat s using an applicator bar with a thickness of 250 μm. The coating was irradiated by UV light at 1 j/cm^2 in the air. The cured films as they

were coated to the glass plates were subjected to a heating test or a heat and light resistant test by ultraviolet exposure (QUV).

(ii) Heating test or heat and light resistant test by ultraviolet exposure (QUV)

The test leaves were placed in a thermostat at 120°C for 7-14 days for the heating test. For the QUV test, the test leaves were exposed to UV light by a ultraviolet exposure device.

(iii) Measurement of the color change

ΔE and YI values of the test leaves were measured using a color difference meter (COLOR ANALYZER TC-1800N) to compare the change in color of the test leaves.

(iv) Measurement of viscosity

Viscosity of the liquid curable resin compositions was measured at 25°C using a B-type viscometer.

The results are shown in Table 5.

TABLE 5

	Example 1		Example 2		Example 3		Example 4		Example 5		Example 6	
	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI
Initial Value	1.2	1.8	1.3	1.9	1.1	1.8	1.0	1.3	1.5	1.6	1.3	1.7
QUV (after 7 days)	1.4	2.7	1.5	2.6	1.3	2.7	1.5	2.1	1.9	2.8	1.5	2.0
120°C (after 14 days)	8.5	14.1	9.4	15.2	8.4	13.4	7.3	14.1	10.1	16.3	7.6	12.9
Viscosity (dPa.s at 25°C)	3000		2300		2200		3200		3800		3000	

TABLE 6

	Example 7		Example 8		Example 9		Example 10		Example 11		Example 12	
	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI
Initial Value	1.3	1.6	1.5	1.9	1.4	1.6	1.5	1.8	1.3	1.5	1.0	1.3
QUV (after 7 days)	1.6	2.4	1.6	2.8	1.9	3.0	2.1	3.3	2.0	2.7	1.8	2.5
120°C (after 14 days)	8.4	13.6	9.4	17.5	9.5	18.1	8.3	19.0	7.9	16.3	9.1	16.1
Viscosity (dPa.s at 25°C)	3800		3300		3200		4000		3300		4000	

TABLE 7

	Comparative Example 1		Comparative Example 2		Comparative Example 3		Comparative Example 4		Comparative Example 5		Comparative Example 6	
	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI	ΔE	YI
Initial Value	1.2	1.8	1.3	1.8	1.0	1.6	1.3	1.6	1.5	1.8	1.3	1.9
QUV (after 7 days)	11.0	19.1	12.5	20.4	11.9	21.3	12.0	17.4	14.4	21.3	12.1	23.1
120°C (after 14 days)	13.5	19.5	13.8	20.1	15.6	23.4	14.0	18.5	15.6	20.8	14.5	23.8
Viscosity (dPa.s at 25°C)	9000		8500		8500		8300		7900		7900	

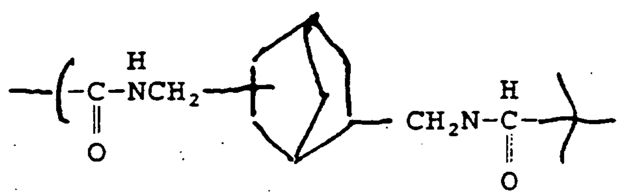
Table 8

	Comparative Example 7		Comparative Example 8	
	ΔE	YI	ΔE	YI
Intitial Value	1.0	1.5	1.1	1.8
QUV (after 7 days)	10.4	17.2	11.9	18.8
120°C (after 14 days)	14.1	19.3	15.2	19.3
Viscosity (dPa.s at 25°C)	8200		8200	

The liquid curable resin composition of the present invention has a low viscosity, exhibits excellent coatability, and produces cured product having superior durability and, particularly, free from coloration due to heat or lights. The composition is suitable as a coating material for optical fiber. In addition, when used as a coating material for woods, plastic materials, and the like, the composition not only exhibits high productivity due to its excellent coatability, but also ensures coatings with prolonged durability.

WHAT IS CLAIMED IS

1. A liquid curable resin composition comprising a urethane (meth)acrylate obtained by the reaction of a polyol, a diisocyanate, and a (meth)acrylate containing a hydroxyl group, and having a structural unit represented by the following formula (1),



(1)

2. The liquid curable resin composition according to claim 1, wherein the diisocyanate is 2,5-bis(isocyanatemethyl)bicyclo[2.2.1]heptane and/or 2,6-bis(isocyanatemethyl)bicyclo[2.2.1]heptane, or a combination of these diisocyanate and other organic diisocyanate.

3. The liquid curable resin composition according to any one of claims 1-2, wherein the urethane (meth)acrylate has a number average molecular weight of about 500-15,000.

4. The liquid curable resin composition according to any one of claims 1-3, containing about 10-90% by weight of the urethane (meth)acrylate.

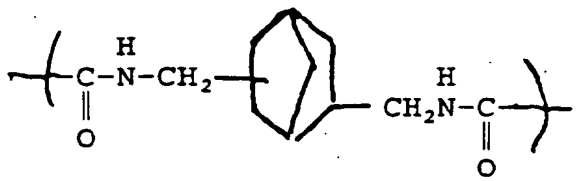
5. The liquid curable resin composition according to any one of claims 1-4, further containing a urethane (meth)acrylate which is a reaction product of one mol of a diisocyanate and two mols of a (meth) acrylate containing a hydroxyl group.

6. The liquid curable resin composition according to any one of claims 1-5, further containing a polymerizable monofunctional vinyl monomer.

7. The liquid curable resin compound according to any one of claims 1-6, further containing a

polymerizable polyfunctional vinyl monomer

8. A radiation curable optical fiber coating composition comprising a urethane (meth)acrylate obtained by the reaction of a polyol, a diisocyanate and a (meth)acrylate containing a hydroxylgroup, and having at least one structure unit represented by the following formula (1)



(1)

9. Coating competition according to claim 8 wherein the composition comprises about 10-90% by weight of the urethane (meth)acrylate, and about 15-80% by weight of polymerizable monomers.

10. Coating composition according to any one of claims 8-9 wherein the composition further comprises about 0.1-10% by weight of polymerization initiator.

11. Coating composition according to any one of claims 8-10 wherein the composition further comprises a silane coupling agent.

12. An optical glass fiber coated with a coating obtained by radiation curing of a composition according to any one of claims 8-11.

INTERNATIONAL SEARCH REPORT

Inter.   nal Application No
PCT/NL 96/00404

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G18/81 C08G18/75 C08G18/67 C08F299/06 G02B6/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C08F G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9427 Derwent Publications Ltd., London, GB; Class A89, AN 94-221869 XP002021926 & JP,A,06 157 451 (MITSUI TOATSU CHEM INC) , 3 June 1994	1,2
Y	see abstract ---	3-10
Y	DATABASE WPI Section Ch, Week 8222 Derwent Publications Ltd., London, GB; Class A25, AN 82-44876E XP002021927 & JP,A,57 067 622 (TOYODA GOSEI KK) , 24 April 1982 see abstract --- -/--	1-10

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
2 January 1997	11. 02. 97

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	EP,A,0 168 173 (CELANESE CORP) 15 January 1986 see page 3, line 29 - page 4, line 39 see claims 1,3	1-10
A	DATABASE WPI Section Ch, Week 9133 Derwent Publications Ltd., London, GB; Class A82, AN 91-242309 XP002021928 & JP,A,03 157 412 (NIPPON KAYAKU KK) , 5 July 1991 see abstract	1-12
A	DATABASE WPI Section Ch, Week 8945 Derwent Publications Ltd., London, GB; Class A82, AN 89-328764 XP002021929 & JP,A,01 244 848 (DAINIPPON PRINTING KK) , 29 September 1989 see abstract	1-12

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/NL 96/00404

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